

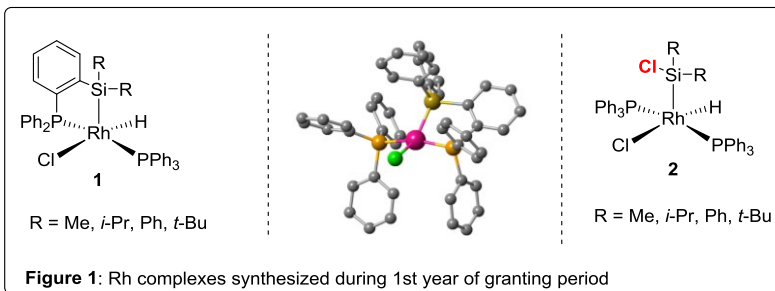
PRF#58845-UNI1

Synthesis of Stable Silyl Rh(III) Hydride Complexes for Alkene Functionalization Reactions

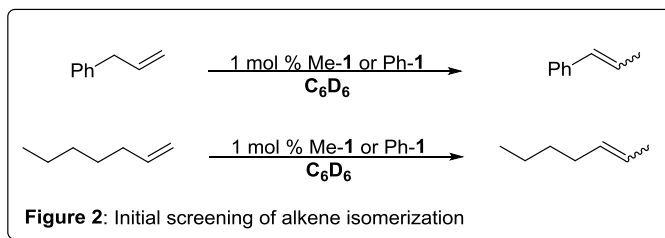
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Year One Narrative Report

In our proposal, we state two clear aims. One: to synthesize chelating $R_2SiPPhenRh(III)-H$ (**1**) complexes; and two, to use these complexes in alkene isomerization/functionalization reactions. At the start of the granting period a new student took the project over, so it was important to have them learn how to synthesize these compounds and the corresponding ligands. Additionally, one of our key hypotheses was that the chelating nature of the compounds renders the Cl-Rh-Si stable to reductive elimination reactions. So it was important to test this hypothesis fully.

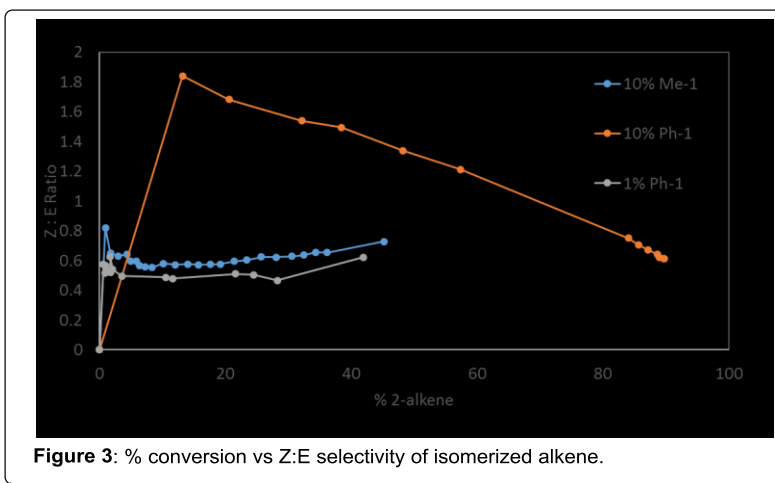


To this end we synthesized complexes **1** and **2** (Figure 1). While Me-**1**, *i*-Pr-**1**, and Ph-**1** were first reported in the original PRF narrative, we have since solved the X-ray crystal structure of Ph-**1**. Additionally while trace amounts of *i*-Pr-**2** and *t*-Bu-**2** could be observed *in situ* via NMR spectroscopy, they could not be isolated and



whatever did form decomposed into a complex mixture of products. Simple dissolution of compounds **1** and **2** in $CDCl_3$ revealed dramatic differences in the two compounds. Complexes Me-**2** and Ph-**2** decomposed within 2 hours via Cl-Si reductive elimination, while the comparable Me-**1** and Ph-**1** were stable for at least 48 hours in solution at room temperature.

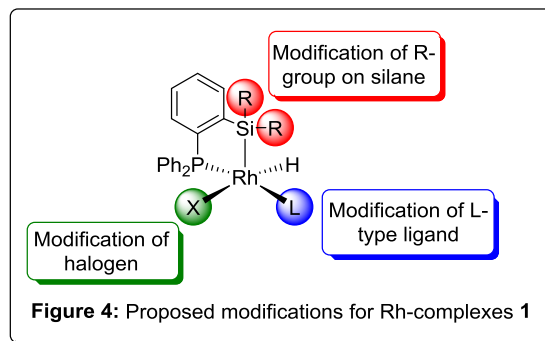
After establishing the stability of Rh-complexes **1**, their competency in alkene isomerization was explored. Specifically treatment of allylbenzene and 1-heptene with either Me-**1** or Ph-**1** yields β -styrene and 2-heptene respectively (Figure 2). Initial conversion for both reaction reveals that these reactions are kinetically selective for the cis alkene. However, in the time that it takes for the reaction to go to full conversion from 1-alkene to 2-alkene (~20 hours) the cis-alkene is



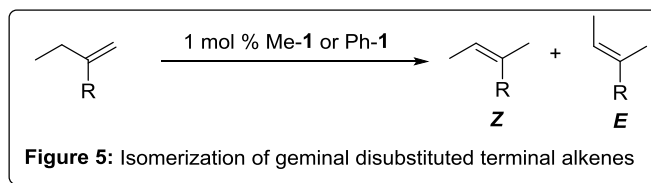
isomerized into the trans alkene. Our best results to date are when 10 mol% Ph-**1** is exposed to 1-heptene at room temperature, at ~20% conversion the cis alkene is favored 2:1 (Figure 3). Initial efforts to optimize the selectivity of this reaction with our current Rh-complexes have been unsuccessful.

Efforts in the second year of the granting period will include the following:

- 1) Synthesizing more Rh-complexes containing P-Si chelating ligands. There is a clear stability benefit to these ligands, when compared to the non-chelating counterparts. In the grant, we propose to synthesize a series of Rh-complexes with substitutions at the positions highlighted in Figure 4. This component of the campaign will now begin in earnest.



- 2) The initial selectivity for the *cis*-alkene inspires us to explore conditions (or substrates) in which the *cis*-alkene can be irreversibly formed. To this end, we will explore the isomerization of geminal-disubstituted terminal alkenes (Figure 5). We propose that initial isomerization will form the *Z*-alkene and the steric bulk of the system will prohibit the newly formed trisubstituted alkene from coordinating to the metal to undergo further isomerization events.



This project has provided a fertile training ground for my students. The students at YSU receive no direct experience in laboratory organometallic chemistry throughout the general curriculum, and have little direct experience in performing air-free chemistry or in the use of a glovebox. All of the students on this project get hands-on experience performing reactions requiring Schlenk-techniques or the use of a glovebox. Additionally, all but one of the students funded on this project has taken or is currently taking the organometallics lecture course here at YSU, and their experience on this project allows them to apply what they learn in class directly in the lab.